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ARTICLE

Synthesized Process of Calcium Ferrite and Effect of TiO_2 and CaTiO_3 in Fe_2O_3 - CaO - TiO_2 System

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Abstract: In order to investigate the phenomenon that the affecting mechanism of high-titanium vanadium-titanium magnetite is caused by separate TiO_2 or by CaTiO_3 formed from TiO_2 and CaO , calcium ferrite was synthesized by pure reagents of Fe_2O_3 and CaO , and the effect of TiO_2 and CaTiO_3 on the formation mechanism of titanium calcium ferrite (FCT) was researched. Different samples were sintered at the temperatures of 1023~1423 K for different time under air atmosphere based on thermodynamics calculations with Factsage 7.0. The phase transformation and microstructure changes in sintered samples were examined through different characterization means including X-ray diffraction and scanning electron microscope-energy disperse spectroscopy. It is found that the formation process of calcium ferrite can be mainly divided into two stages. The synthesized product is $\text{Ca}_2\text{Fe}_2\text{O}_5$ with the reaction " $\text{Fe}_2\text{O}_3(\text{s}) + 2\text{CaO}(\text{s}) = \text{Ca}_2\text{Fe}_2\text{O}_5(\text{s})$ " between Fe_2O_3 and CaO at 1023~1223 K in the former stage, and the predominant product is CaFe_2O_4 with the reaction " $\text{Ca}_2\text{Fe}_2\text{O}_5(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) = 2\text{CaFe}_2\text{O}_4(\text{s})$ " between $\text{Ca}_2\text{Fe}_2\text{O}_5$ and Fe_2O_3 at 1223~1423 K in the latter stage, in which the reaction rate is accelerated especially at 1423 K. It is observed that CaTiO_3 increases with increasing the temperature. However, the solid solution of Ti element in calcium ferrite is greatly difficult to realize and the reaction between TiO_2 and calcium ferrite is not an effective way to generate FCT. It is also observed that the amount of Fe element in the phase boundary of CaTiO_3 and FCT increases with the extension of the thermal insulation time. FCT is predominantly formed through the solid solution of Fe component in CaTiO_3 , and the main reaction is " $\text{Fe}_2\text{O}_3(\text{s}) + \text{CaTiO}_3(\text{s}) = \text{FCT}(\text{s})$ ".

Key words: calcium ferrite; sintering; TiO_2 ; CaTiO_3 ; Fe_2O_3 - CaO - TiO_2 system

Vanadium-titanium magnetite, rich in iron, titanium, vanadium, etc, has significant comprehensive utilization value and is used widely in the blast furnace iron-making and latter vanadium-extracting industry in China so far^[1-6]. It has been reported comprehensively that the tumbler strength, rate of finished products and low temperature reduction and pulverization rate of vanadium-titanium magnetite sinters are greatly poor, and previous studies have indicated that TiO_2 has great reverse effects on the sinter quality of vanadium-titanium magnetite^[7,8]. However, researchers have different opinions on the affecting mechanism of vanadium-titanium

magnetite sinters^[8,9] and it is still unclear that the deterioration of sinter property is caused by separate TiO_2 or CaTiO_3 formed from TiO_2 and CaO .

For ordinary iron ores, it is commonly affirmed that the strength increasing of iron ore sinters has great relations with the generation of calcium ferrite, and calcium ferrite theory provides theoretical basis for the production of modern high basicity sinters with good quality^[10-12]. However, for vanadium-titanium magnetite ores, calcium ferrite is evidently found less but perovskite (CaTiO_3), Fe-bearing anosovite ($\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Ti}_2\text{O}_5$) are obviously found because of the existence of TiO_2 in the

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sinters, contributing to the complexity of sintering consolidation and liquid reaction mechanism. Since calcium ferrite theory cannot explicitly illustrate the low strength, poor quality and especially serious reduction degradation, the challenge is proposed for the applicability of traditional calcium ferrite theory. Consequently, it is necessary to research the effect of TiO_2 and CaTiO_3 on the formation mechanism of titanium-bearing calcium ferrite.

High-titanium vanadium-titanium magnetite ores have relatively far higher titanium contents compared with ordinary vanadium-titanium magnetite^[13]. As the largest high-titanium vanadium-titanium magnetite, 20 billion tons of reserves have just been explored in Chaoyang District in Liaoning of China in recent several years, which accounts for more than half of total vanadium-titanium magnetite resources in China. Large-scale exploitation and utilization of these mineral resources have seldom been carried out so far due to the poor-quality sinters and immature utilization technology. Compared with ordinary vanadium-titanium magnetite, the influencing of titanium oxide on vanadium-titanium magnetite is more highlighted.

According to the theory of calcium ferrite, researchers have done lots of work focusing on the optimization of sinters for ordinary iron ores. Ding et al have studied the formation mechanism of silicon-ferrite of calcium (SFC) by solid-state reactions in order to understand the process of SiO_2 involved in the formation of complex silico-ferrites of calcium and aluminum^[14], and Pownceby et al have investigated the solid solution limits, thermal stability and selected phase relationships within the Fe_2O_3 - CaO - SiO_2 (FCS) system^[15]. Wang et al have researched the formation characteristics of calcium ferrite in low silicon sinter^[16]. Nakashima et al have researched the effects of adding SiO_2 or Al_2O_3 on the wetting and penetration characteristics of calcium ferrite melts, $\text{CaO}\cdot\text{Fe}_2\text{O}_3$ (CF) and $\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$ (CF_2) in sintered hematite^[17]. Besides, Jeon has studied the formation of calcium ferrites by solid state reactions between different kinds of iron oxides (Fe_2O_3 , Fe_3O_4 and wustite) and CaO under various oxygen potentials at 1273 K^[18]. Yu et al have investigated the wetting behavior of MgO -doped and Al_2O_3 -doped calcium ferrites^[19,20]. In addition, studies on the thermodynamic investigation^[21] and isothermal and non-isothermal reduction kinetics of MgO -doped, Al_2O_3 -doped and SiO_2 -doped calcium ferrites have been carried out^[11,22-24]. However, systematic studies on the formation mechanism of vanadium-titanium magnetite including high-chromium vanadium-titanium magnetite and high-titanium vanadium-titanium magnetite has been elusive. Chen et al has carried out the work on the diffusion behavior between Cr_2O_3 and calcium ferrite in order to provide theoretical basis for the utilization of high-chromium vanadium-titanium magnetite^[25], and Ding et al have investigated the reaction sequence and formation kinetics of perovskite by calcium ferrite-titania reaction^[26]. However, effect of TiO_2 or formed CaTiO_3 on the formation of calcium ferrite in Fe_2O_3 - CaO - TiO_2 (FCT) system is still unclear. Thus, it is essential and significant to figure out the effects of TiO_2 and CaTiO_3 on the formation mechanism of FCT phase.

In this study, the synthesized process of calcium ferrite was first studied by pure reagents of Fe_2O_3 and CaO , and the effect of TiO_2 and CaTiO_3 on the formation mechanism of FCT was further investigated. It is expected to provide theoretical guidance for vanadium-titanium magnetite sinter, especially high-titanium vanadium-titanium magnetite sinter.

1 Experiment

1.1 Experimental materials and methods

The pure reagents of Fe_2O_3 , TiO_2 and CaO , provided by Sinopharm Chemical Reagent Co., Ltd, were adopted as the raw materials. The raw materials were weighed according to the ingredient scheme in Table 1, and mixed for 12 h with the agate ball. For each experimental sample, 3 g mixed materials were taken and pressed into a cylinder with the diameter of 8 mm and the height of 5 mm by briquetting machine under the pressure of 2.0 MPa for 2 min. The prepared samples were placed in the alumina crucible with 15 mm in diameter and 20 mm in height and then put in the Box-type atmosphere furnace for sintering with the temperature regime shown in Fig. 1. Different samples were sintered and prepared in the selected temperatures of 1023, 1123, 1223, 1323 and 1423 K under air atmosphere.

1.2 Characterization methods

In this study, the sintered samples were ground to 0.05 mm in the grinding machine for X-ray diffraction (X-ray diffraction) analysis by X'pert pro (Panalytical, Almelo, the Netherlands) with $\text{Cu K}\alpha$ radiation, and sanded and polished to a smooth surface for SEM examination and EDS analysis (scanning electron microscopy-energy dispersive spectroscopy, Ultra Plus; Carl Zeiss GmbH, Jena, Germany). XRD, SEM and EDS were used for the mineral phase analysis, the

Table 1 Ingredient scheme of solid-reaction (wt%)

Sample	Composition of raw materials			Content of elements		
	Fe_2O_3	CaO	TiO_2	Fe	Ca	Ti
1#	51	49	0	35.7	35	0
2#	49	43	8	34.3	30.7	6

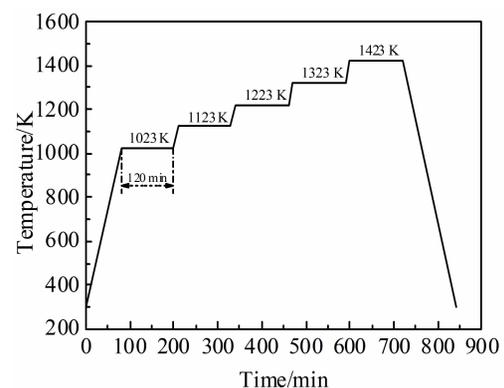


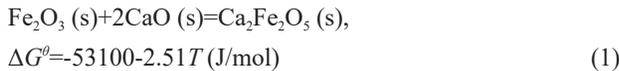
Fig.1 Heating curve of sintering for different samples

microscopic morphology examination and micro-area component investigation, respectively.

2 Results and Discussion

2.1 Formation process of calcium ferrite

Solid reaction is the most vital approach for the formation of FC, and the conditions of the solid reaction determine the phase types. Fig. 2 describes XRD patterns of sample 1# (51wt%Fe₂O₃-49wt%CaO) sintered at 1023, 1123, 1223, 1323 and 1423 K for 2 h under air atmosphere. The results show that Ca₂Fe₂O₅ (C₂F) appears at 1023 K, and the formation of C₂F is due to the reaction of Fe₂O₃ and CaO, as shown in Eq.(1).



The value of diffraction peak of Ca₂Fe₂O₅ increases obviously with increasing the temperature, and some relatively weak diffraction peaks of Ca₂Fe₂O₅ (C₂F) appear once again when the temperature increases to 1223 K, from which it is also indicated that the content of Ca₂Fe₂O₅ increases as the temperature increases. Furthermore, the phase of CaFe₂O₄ appears at 1123 K and the content of CaFe₂O₄ begins to increase at 1223 K observably from XRD results. Ding et al^[27] studied SiO₂ involved in the formation process of SFC by adopting XRD, in which it is reported that Ca₂Fe₂O₅ begins to form at 973 K while CaFe₂O₄ appears at 1073 K approximately. In this study, talking the phase existence of Ca₂Fe₂O₅ at 1023 K (>973 K) and CaFe₂O₄ at 1123 K (>1073 K) does not represent to deny the lowest forming temperature, and it is mainly aimed at illustrating the formation process of C₂F in

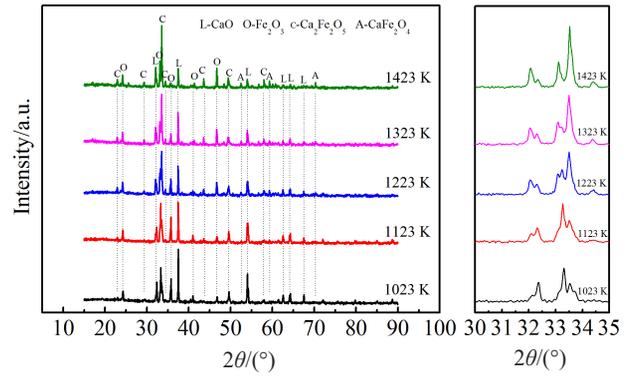


Fig.2 XRD patterns of sample 1# (51wt% Fe₂O₃-49wt% CaO) sintered from 1023 K to 1423 K for 2 h under air atmosphere

the temperature range of 1023~1223 K and that of CF at 1223~1423 K, in which both temperature ranges are higher than the lowest forming temperature of C₂F (973 K) and CF (1073 K) reported in Ding's study. In future study, the lowering temperature and temperature range will be researched.

Fig. 3 shows SEM images of microscopic structures of sample 1# (51wt% Fe₂O₃-49wt% CaO) sintered at 1023 and 1423 K for 2 h under air atmosphere. The voids and holes in Fig.3c are formed probably because solid particles that do not participate in the reaction are dropped from the reacted sample during SEM-EDS sample preparation. Through the microscopic structures analysis of samples, it can be found that the bonding phase is mainly Ca₂Fe₂O₅ (FC₂) at 1023 K, and there are still intermediate mixing phases (circled part in Fig.3b and

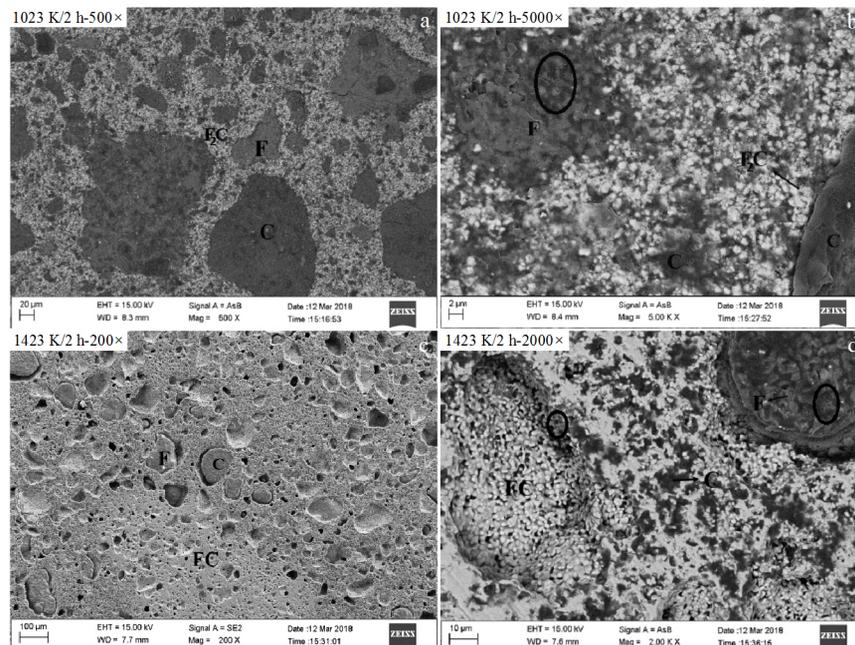


Fig.3 SEM images of microscopic structures for sample 1# (51wt%Fe₂O₃-49wt%CaO) sintered at 1023 K (a, b) and 1423 K (c, d) for 2 h under air atmosphere

3d) containing Fe^{3+} , Ca^{2+} and O^{2-} for forming calcium ferrite phases. Due to solid-state reaction, $\text{Ca}_2\text{Fe}_2\text{O}_5$ will continue to react with Fe_2O_3 which is not involved in the reaction in the case that Fe_2O_3 is abundant. The reaction process between FC_2 and Fe_2O_3 is given by Eq.(2).

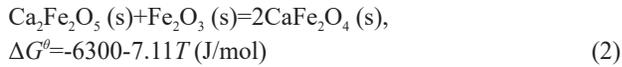
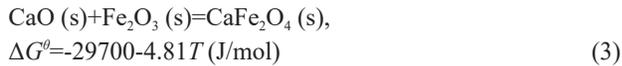


Fig.4a and 4b show EDS results of sample 1# sintered at 1023 and 1423 K, respectively, in which areas A and B are FC_2 and FC phases, respectively. It is easy to find that the content of Fe element in the generated FC_2 is low at 1023 K. When the temperature increases to 1423 K, the content of Fe element in the generated FC_2 increases significantly, which indicates that Fe_2O_3 continues to participate in the formation process of FC with increasing the temperature.

Through above analyses, it can be concluded that the formation of calcium ferrites is dynamic, and this process is mainly divided into three steps. The first step is the reaction between Fe_2O_3 and CaO at 1023 K, and the reaction product is $\text{Ca}_2\text{Fe}_2\text{O}_5$, as shown in Eq.(1). When the temperature increases to 1223 K, the reaction in the second step between $\text{Ca}_2\text{Fe}_2\text{O}_5$ and Fe_2O_3 begins to occur, and the main product is CaFe_2O_4 , as shown in Eq. (2). The reaction in the third step happens also between Fe_2O_3 and CaO at 1223 K, but what's different from the first step is that the resultant is CaFe_2O_4 , as shown in Eq.(3).



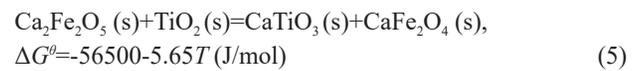
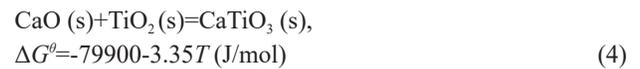
And the third reaction rate is accelerated when the temperature increases to 1423 K. Temperature is a very important factor in the generating process of FC. With the increase of temperature, the thermodynamic conditions are improved actively, and the solid reaction rate is accelerated. It is a pivotal cause of temperature influencing the reaction process.

2.2 TiO_2 role in generating process of FCT

Fig. 5 shows XRD patterns of samples 2# (8wt% TiO_2 -49wt% Fe_2O_3 -43wt% CaO) that were sintered from 1023 K to 1423 K for 2 h under air atmosphere. The results show that there are small amounts of CaTiO_3 (CT) and $\text{Ca}_3\text{Fe}_2\text{TiO}_8$

(FCT) at 1023 K besides $\text{Ca}_2\text{Fe}_2\text{O}_5$ (C_2F) and CaFe_2O_4 (FC). Moreover, the peak intensity of CaTiO_3 and $\text{Ca}_3\text{Fe}_2\text{TiO}_8$ (FCT) (at 2θ of about 47° and 60°) increases as the temperature increases, indicating that the contents of CaTiO_3 (CT) and $\text{Ca}_3\text{Fe}_2\text{TiO}_8$ (FCT) increase with increasing the temperature.

Besides, $\text{Ca}_2\text{Fe}_2\text{O}_5$ (C_2F) phase content increases to some extent, which is consistent with the previous description. The increase of CaTiO_3 is in accordance with previous study on the relationship between the contents of CaTiO_3 and temperature^[28]. For TiO_2 , the most important way to participate is in the reaction process between TiO_2 and CaO , and CaTiO_3 is directly produced (Eq. (4)). For $\text{Ca}_2\text{Fe}_2\text{O}_5$ (C_2F), the reaction between TiO_2 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ (C_2F) (Eq.(5)) cannot be ignored.



From thermodynamics calculation, Eq.(5) is much easier to occur than other reactions (Fig.11). In other words, because of reaction of Eq. (5), although $\text{Ca}_2\text{Fe}_2\text{O}_5$ (C_2F) is generated in Eq. (1), some $\text{Ca}_2\text{Fe}_2\text{O}_5$ products are consumed again sometimes, contributing to the slow increasing content of $\text{Ca}_2\text{Fe}_2\text{O}_5$ (C_2F). Another unsolved problem is the generating progress of $\text{Ca}_3\text{Fe}_2\text{TiO}_8$ (FCT), which will be further discussed.

Fig. 6 shows SEM images of microscopic structures of samples 2# that were sintered from 1023 K to 1423 K for 2 h under air atmosphere. It is observed that the content of the bonding phase increases gradually as the temperature increases. Besides, layers are present around FC when the temperature increases to 1223 K (Fig. 6a-6c), so it can be determined that the composition of the layer is FCT through EDS analysis shown in Fig. 7. The appearance of FCT layer has an important guiding role in understanding the effect of TiO_2 on the formation of FCT. There are two main approaches to form FCT layers that are present around FC. The first approach is the reaction between FC and TiO_2 , and the second approach is the reaction between Fe_2O_3 and CT. However, the significant question that how FC is involved in FCT generating is unclear. Thus, these two important processes will

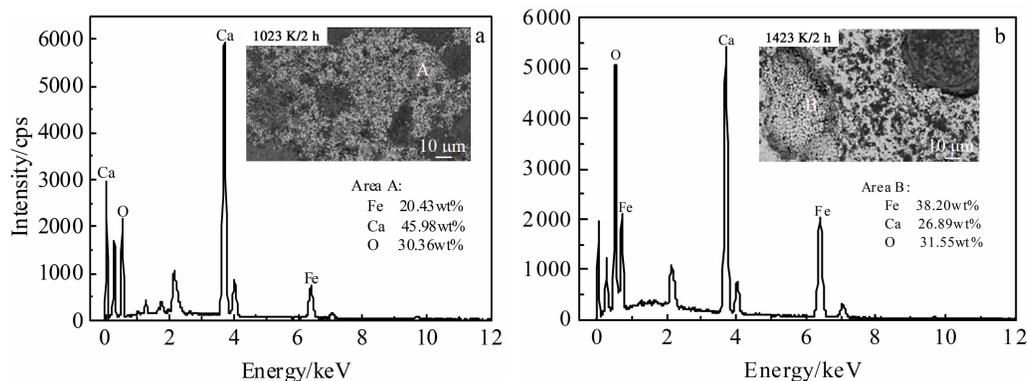


Fig.4 EDS analysis results of FC phases for sample 1# sintered at 1023 K (a) and 1423 K (b)

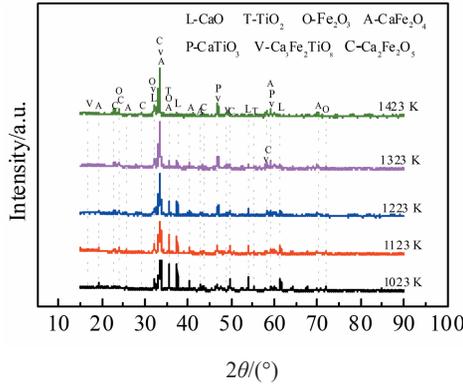


Fig.5 XRD patterns of samples 2# sintered at 1023~1423 K for 2 h under air atmosphere

be further elaborated in the following studies.

2.3 Calcium ferrite role in generating process of FCT

In order to further determine how calcium ferrite is involved in the generating of FCT, reaction experiments between calcium ferrite and TiO_2 were carried out at 1423 K for 2 h, in which calcium ferrite was obtained by solid reaction at 1473 K for 4 h under air atmosphere, according to XRD pattern in Fig.8, and XRD results of the experiment are shown in Fig.9. From the results, the products include $CaTiO_3$ (CT), $Ca_2Fe_2O_5$ (C_2F) and $Ca_3Fe_2TiO_8$ (FCT). In the process of preparing FC, parts of Fe_2O_3 and CaO are not fully involved in the reaction. As the particle sizes of Fe_2O_3 and CaO are not inhomogeneous, contactile parts preferentially react while non-exposed parts have no chemical changes in a certain reaction time. Therefore, partial $CaTiO_3$ (CT) phases in the experiment

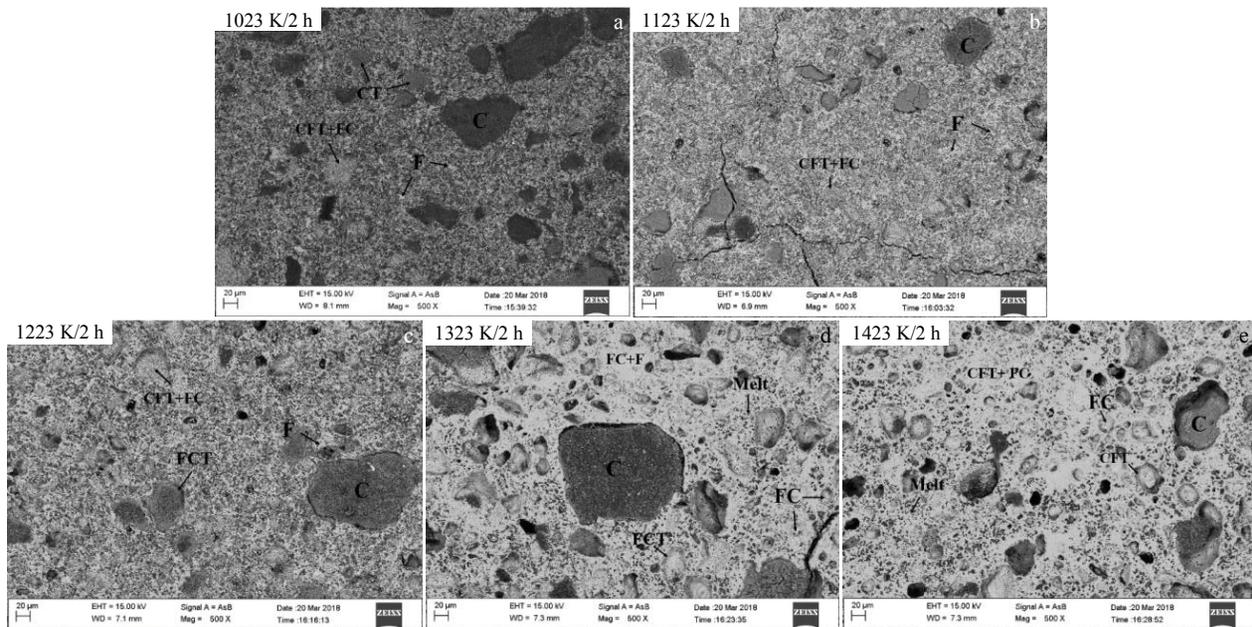


Fig.6 SEM images of samples 2# sintered at different temperatures for 2 h under air atmosphere: (a) 1023 K, (b) 1123 K, (c) 1223 K, (d) 1323 K, and (e) 1423 K

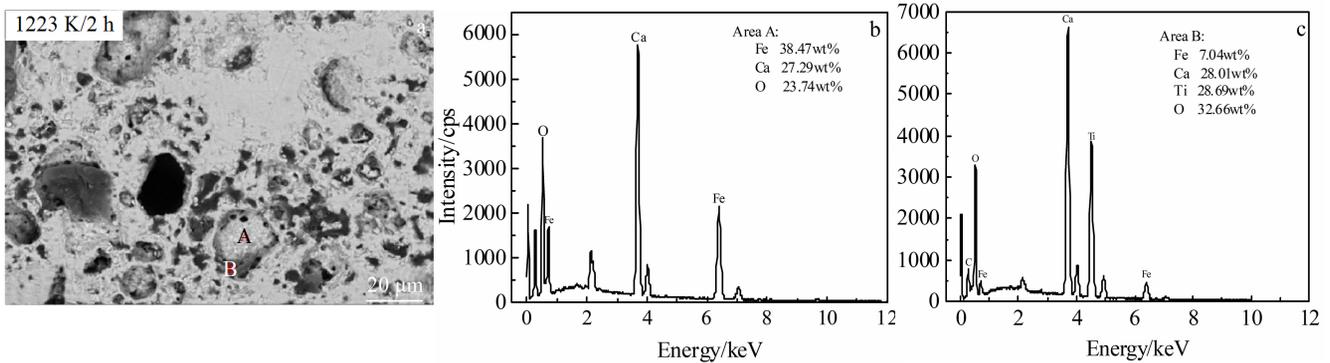


Fig.7 SEM image (a) and EDS analysis of area A (b) and area B (c) in Fig.7a for the sample sintered at 1223 K for 2 h under air atmosphere

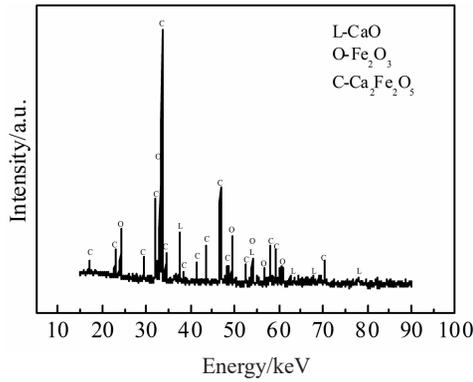


Fig.8 XRD patterns of FC sintered at 1473 K for 4 h under air atmosphere

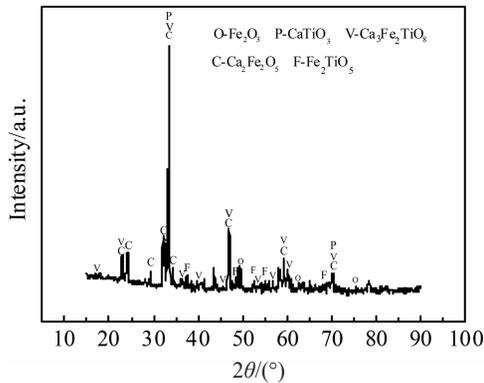


Fig.9 XRD pattern of the reaction product between FC and TiO₂ carried out at 1423 K for 2 h

are caused by the reaction between TiO₂ and CaO, and partial FCT phases in the experiment are caused by the reaction between Fe₂O₃, TiO₂ and CaO. The source of Ca₂Fe₂O₅ (C₂F) phase comes from the reaction between Fe₂O₃ and CaO.

Fig. 10 shows the EDS analysis results for the reaction between calcium ferrite and TiO₂ that was carried out at 1423 K for 30, 60 and 120 min. From the results, it is easy to find that the content of Ti element is very low and it gradually increases as the reaction time is prolonged, which means that the solid solubility of Ti element in calcium ferrite is limited. In other words, it is very difficult to generate FCT by the reaction between calcium ferrite and TiO₂ because the solid solution process of Ti element in calcium ferrite is greatly difficult to realize.

Fig. 11 shows relationships between Gibbs free energy change and reaction temperature (the thermodynamics data was taken from Factsage 7.0). In terms of thermodynamics, the Gibbs free energy for Eq. (6), namely, for the reaction between CaFe₂O₄ and TiO₂, is much lower than that of other reactions at the same temperature, indicating that reaction of Eq.(6) is easier to realize in the temperature increase process.

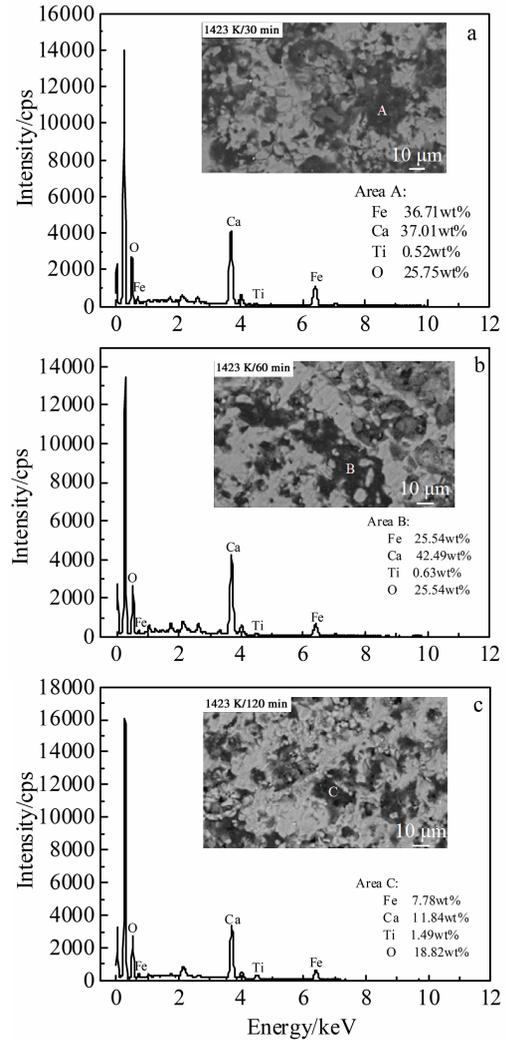


Fig.10 EDS analyses of area A (a), area B (b) and area C (c) for the reaction between FC and TiO₂

Therefore, although FCT is not formed by the reaction between TiO₂ and FC, Eq. (6) at 1423 K is facilitated.

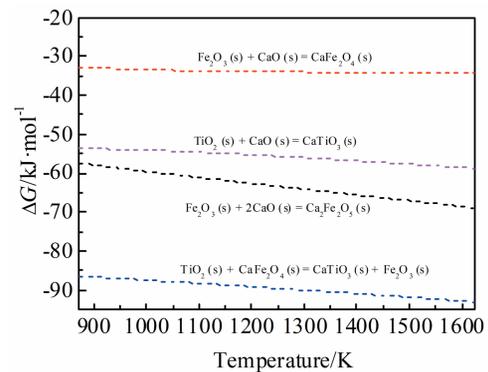
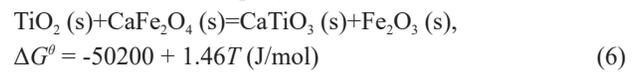


Fig.11 Thermodynamics data for different reactions

2.4 CaTiO₃ role in generating process of FCT

In order to understand clearly the role of CaTiO₃ in the generating process of FCT, the reaction between CT and Fe₂O₃ was carried out at 1423 K for different time. Fig. 12 shows XRD results of the reaction between CT and Fe₂O₃ at 1423 K

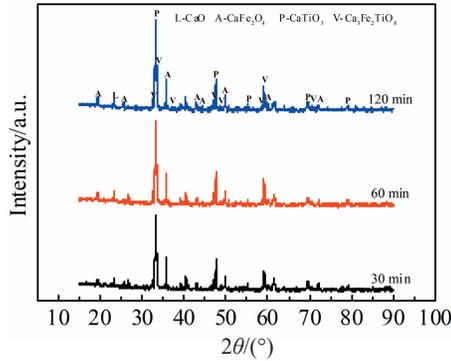


Fig.12 XRD patterns for reaction between CT and Fe₂O₃ at 1423 K for 30, 60 and 120 min

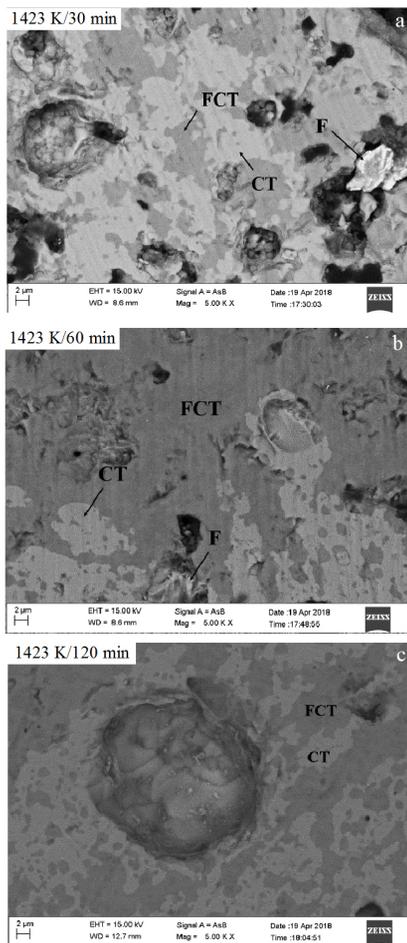


Fig.13 SEM images of samples sintered at 1423 K for 30 min (a), 60 min (b) and 120 min (c)

for 30, 60 and 120 min. The results show that the products are mainly FCT, and it is indicated that another main route of the formation of FCT is through the reaction between CT and Fe₂O₃.

The SEM images of microscopic structures of different samples that were sintered at 1423 K for 30, 60 and 120 min are shown in Fig.13 and EDS results of FCT phases (areas A, B and C) are shown in Fig.14. It can be found that the amount of Fe element in FCT gradually increases with extension of thermal insulation time. Similarly, EDS line scanning analysis in Fig.15 shows the phase boundary between CT and FCT at 1423 K, which also shows similar experimental result. It is observed that the amount of Fe element in the phase boundary of CT and FCT increases with the extension of the thermal insulation time.

The above analysis shows that the crucial way to generate FCT is the solid solution of Fe in CaTiO₃ (CT). It is probably as a result of the fact that Fe occupies the position of Ti in crystal lattice in the formation of FCT. The reaction process

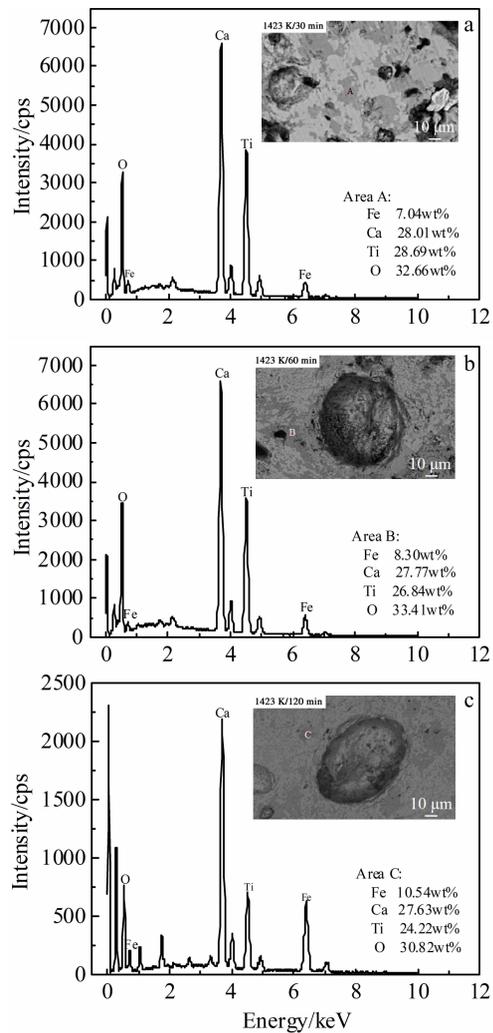


Fig.14 EDS results of FCT phases for samples sintered at 1423 K for 30 min (a), 60 min (b) and 120 min (c)

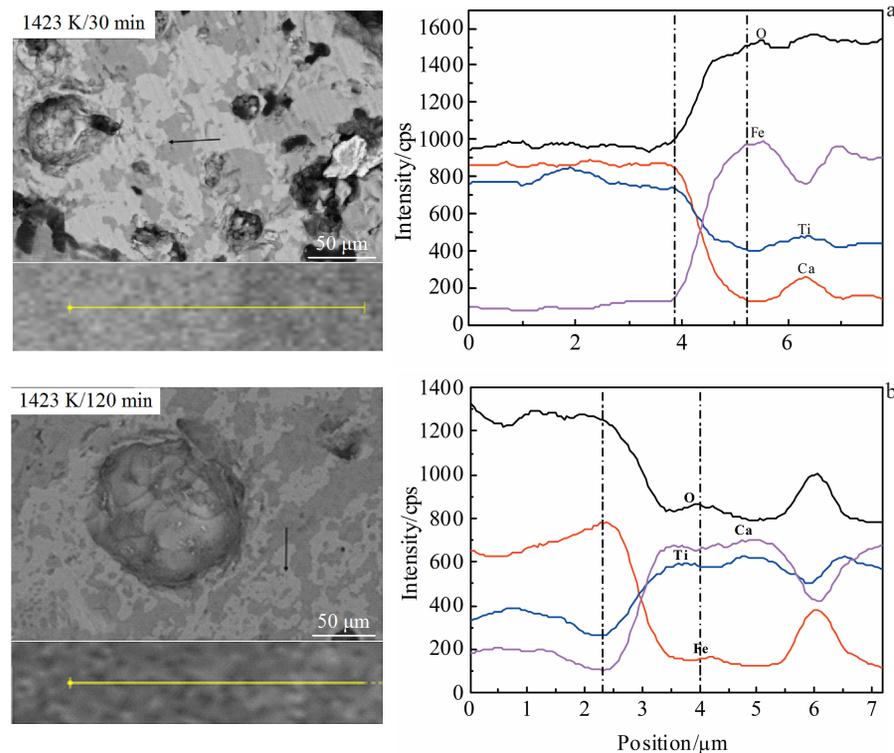
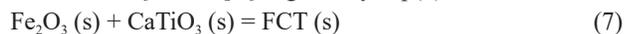


Fig.15 EDS line scanning results of the phase boundary between CT and FCT at 1423 K for 30 min (a) and 120 min (b)

between CaTiO_3 and Fe_2O_3 is given by Eq.(7).



3 Conclusions

1) The formation process of calcium ferrite (FC) can be divided into two stages. The reaction product is $\text{Ca}_2\text{Fe}_2\text{O}_5$ between Fe_2O_3 and CaO at 1023~1223 K in the former stage. The predominant product is CaFe_2O_4 for the reaction between $\text{Ca}_2\text{Fe}_2\text{O}_5$ and Fe_2O_3 at 1223~1423 K in the latter stage, in which the reaction rate is accelerated especially at 1423 K.

2) The reaction between TiO_2 and FC is not an effective way to generate titanium calcium ferrite (FCT) at 1423 K because the solid solution of Ti element in FC is greatly difficult to realize. TiO_2 is mainly involved in reaction $\text{TiO}_2 (\text{s}) + \text{CaFe}_2\text{O}_4 (\text{s}) = \text{CaTiO}_3 (\text{s}) + \text{Fe}_2\text{O}_3 (\text{s})$ at 1423 K.

3) The main reason for the formation of FCT is the solid solution of Fe element in CaTiO_3 , and the main reaction is that FCT is generated by Fe_2O_3 and CaTiO_3 .

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Fe₂O₃-CaO-TiO₂体系下铁酸钙的合成过程及TiO₂和CaTiO₃的影响

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摘要: 为了确定高钛型钒钛磁铁矿烧结过程中铁酸钙的生成是受TiO₂还是TiO₂和CaO形成的CaTiO₃影响, 首先利用Fe₂O₃和CaO的纯试剂合成了铁酸钙, 并研究了TiO₂和CaTiO₃对钛铁酸钙(FCT)形成的影响。在Factsage 7.0软件进行热力学计算的基础上, 通过在空气气氛下进行烧结, 获得了在1023~1423 K温度范围内、不同烧结时间的不同样品。通过X射线衍射和扫描电镜-能谱分析等表征手段, 对烧结样品的物相转变和微观结构变化进行了表征。发现FCT的形成过程主要分为2个阶段: 前一阶段为1023~1223 K温度范围内Fe₂O₃与CaO之间的反应, 合成产物为Ca₂Fe₂O₅, 反应方程式为“Fe₂O₃(s)+ 2CaO(s)= Ca₂Fe₂O₅(s)”; 后一阶段为1223~1423 K温度范围内Ca₂Fe₂O₅和Fe₂O₃的反应, 主要产物为CaFe₂O₄, 反应为“Ca₂Fe₂O₅(s)+ Fe₂O₃(s)= 2CaFe₂O₄(s)”, 该阶段尤其是温度为1423 K时, 反应速率显著加快, 随温度的升高CaTiO₃显著增加。然而, Ti元素在铁酸钙中的固溶很难实现, TiO₂与铁酸钙之间的反应不是形成FCT的有效途径。随着保温时间的延长, CaTiO₃和FCT相界中Fe元素含量增加。FCT主要是通过Fe组分在CaTiO₃中固溶形成的, 主要反应是“Fe₂O₃+CaTiO₃(s)=FCT(s)”。

关键词: 铁酸钙; 烧结; TiO₂; CaTiO₃; Fe₂O₃-CaO-TiO₂体系

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